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Generation of alkyl fragments on Rh/SiO_2 and VO_x-promoted Rh/SiO_2

A. Trunschke [1] and H. Knözinger

Institut für Physikalische Chemie, Universität München, Sophienstrasse 11, 8000 Munich 2, Germany

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The adsorption of ethylene on Rh/SiO_2 and $Rh-VO_x/SiO_2$ has been studied by transmission FTIR spectroscopy. For C_2H_4 chemisorption at 298 K on Rh/SiO_2 molecularly adsorbed C_2H_4 and ethylidyne species are identified. It has been found that ethylidyne can be hydrogenated toward surface ethyl species in a reversible reaction at room temperature. On $Rh-VO_x/SiO_2$ the fragmentation of C_2H_4 into methylene species has been observed during C_2H_4 adsorption at 298 K.

Keywords: Rhodium; ethylene; ethylidyne; VO_x-promoter

1. Introduction

Chemisorbed hydrocarbon species such as methylene, methyl or ethyl are prominent intermediates in a number of metal catalyzed reactions like hydrogenation, dehydrogenation, and isomerization. Alkyl fragments have also been proposed as surface species formed in the course of Fischer–Tropsch reaction: alkyl migration, i.e. CO insertion into a $M-CH_3$ or $N-CH_2CH_3$ bond has been shown to be an elementary step in the synthesis of C_2-oxygenates, e.g. ethanol, or C_3-oxygenates, e.g. propanol, from CO and H_2 [1,2]. Among the different catalytic systems, oxide supported rhodium catalysts, promoted with early transition metals such as vanadium or manganese are the most suitable for the selective formation of oxygenates in CO hydrogenation (e.g. refs. [3,4]). The spectroscopic identification of adsorbed species and the study of their reactivities during CO insertion reaction could provide an essential basis for the understanding of the role of promoters in the oxygenate synthesis from CO and H_2.

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[1] On leave from Zentralinstitut für Physikalische Chemie, Rudower Chaussee 5, O-1199 Berlin, Germany.

In the present study we have performed experiments with ethylene adsorption and hydrogenation of the adsorbed species at 298 K on Rh/SiO_2 and Rh–VO_x/SiO_2 in order to generate well defined alkyl fragments for further elucidation of the mechanistic steps involved in CO hydrogenation.

The adsorption forms and decomposition reactions of ethylene on rhodium single crystals have been extensively investigated in a wide temperature range from 77 K to above 800 K [5–9]. In contrast, there are far less examples of systematic studies on oxide supported rhodium, due to the often complex situation caused by the possible coexistence of a multiplicity of adsorbed species [10–13]. At low temperature ethylene is mainly adsorbed in a molecular form, while it undergoes dehydrogenation to ethylidyne (CCH_3) as the stable surface species at room temperature. π or di-σ bonded ethylene, both of a nondissociative nature, have been proposed as precursors for ethyl groups on Rh single crystals [8]. Recently, ethyl formation through hydrogenation of C_2H_4(ads.) has been observed by infrared spectroscopy on Pt/SiO_2 [14]. The results of the present work prompted us to assume that ethyl groups can be formed through hydrogenation of ethylidyne species at 298 K on Rh/SiO_2.

2. Experimental

2.1. CATALYSTS

The rhodium catalysts were prepared by impregnation of the silica support (SiO_2, Alpha Products, 340 m^2/g) with a methanolic solution of $RhCl_3 \cdot 3H_2O$ (Johnson Matthey Chemicals LTD). The solvent was evaporated at 310 K at a pressure around 2.5 kPa. The impregnated support was dried for 12 h at 383 K and ground in an agate mortar before calcination in air at 573 or 773 K for 7 h. The nominal Rh content was 3.8 wt%.

The vanadium containing samples were made by impregnation of the silica with an aqueous solution of NH_4VO_3. The precursor was decomposed by heating the samples in air for 3 h at 773 K. This material was then impregnated with $RhCl_3$ and calcined in the same way as described for the pure rhodium catalysts. The promoted catalysts contained formally 3.3 wt% rhodium and 6.8 wt% vanadium corresponding to an atomic ratio V/Rh equal to 4.2.

2.2. INFRARED SPECTROSCOPY

For infrared experiments, the samples were pressed into thin wafers (10–20 mg cm^{-2}) and placed in an infrared cell equipped with CaF_2 windows. The design of the cell, which allows in situ pretreatment at high temperature and low temperature adsorption (80 K) of probe molecules, has been described elsewhere [15]. The adsorption of 10–15 mbar C_2H_4, or H_2 (equilibrium pressure) has been performed after in situ reduction for 2 h in flowing H_2 at 673 K, followed by evacuation for 1 h at 673 K. The gases were obtained from Messer Griesheim (C_2H_4, 99.95%) and Linde. Ethylene was used without further purification, while H_2 was passed through an oxisorb cartridge to remove traces of oxygen and water. All spectra have been recorded with a Bruker FTIR spectrometer (IFS 66) operating at 2 cm^{-1} resolution.

3. Results and discussion

3.1. Rh/SiO_2

Ethylidyne is the predominating product of C_2H_4 chemisorption at 293 K. The spectra obtained after adsorption of 10 mbar ethylene on Rh/SiO_2 at room temperature, followed by evacuation, are shown in figs. 1a–1c. Rh_3CCH_3 is characterized by the intense symmetric C–H stretching mode of the methyl group at 2886 cm^{-1} and the corresponding asymmetric stretch at 2936 cm^{-1}. Peaks at 1341, 1411, and a weak broad feature near 2800 cm^{-1} are considered to be due to the symmetric and asymmetric CH_3 bend and the first overtone of the latter, respectively [10,12]. However, the assignment of the band around 2800 cm^{-1} to an ethylidyne peak has been questioned by Yates et al. in previous papers on C_2H_4 adsorption on Pt/Al_2O_3 [16].

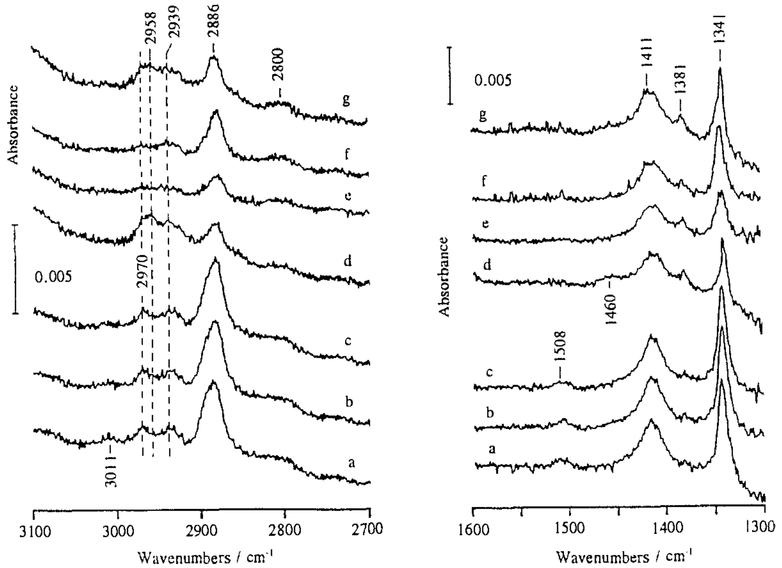


Fig. 1. Infrared spectra of ethylene adsorbed on Rh/SiO_2 at room temperature: (a) after brief evacuation; (b) after evacuation for 60 s; (c) after evacuation for 300 s; (d) after exposure in 10 mbar H_2; (e) after subsequent evacuation for 60 s; (f) after evacuation for 300 s; (g) after second exposure in 10 mbar H_2.

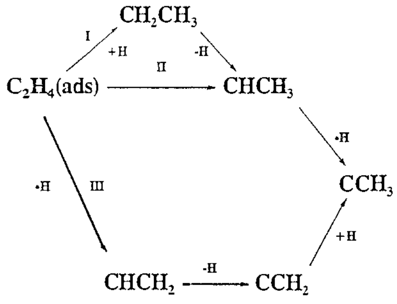
Table 1
Vibrational frequencies (in cm^{-1}) of low temperature adsorption forms of ethylene on Rh and Pt surfaces

Surface	Surface species	$\nu_{as}(CH_2)$	$\nu_{sym}(CH_2)$	$\nu(CC)$/ $\delta(CH_2)$	$\delta(CH_2)$/ $\nu(CC)$	Ref.
Pt/SiO_2	π	–	3016	1496	–	[24]
Rh/Al_2O_3	π	–	–	1499	1214	[13]
Rh/Al_2O_3	π	3080	2966	1509	1222	[10,25]
Rh(111)	BO [a] = 1.52	3080	3000	1485	1200	[9]
Rh(100)	BO = 1.16	3015	2905	1475	1195	[9]
Rh/SiO_2	π	3011	2970	1508	–	this work
Rh/Al_2O_3	di-σ	–	–	[1460]	–	[13]
Pt/SiO_2	di-σ	–	2922	[1428]	–	[24]
Pt/Al_2O_3	di-σ	–	2912	[1427]	–	[10,25]

[a] Bond order.

The vibrational modes at 3011, 2970, and 1508 cm^{-1} seen in spectra a–c of fig. 1 indicate the additional presence of non-dissociatively bonded ethylene. Vibrational frequencies of some examples of molecularly adsorbed ethylene on different metal surfaces, classified in accordance with the two general types of molecular bonding of ethylene, namely π- and di-σ-bonding, are listed in table 1. The di-σ- as well as the π-coordination is realized through a donor–acceptor interaction between the occupied bonding and non-occupied antibonding π-orbitals of ethylene on the one site, and the empty and filled d orbitals of the metal on the other site. This interaction leads to more or less rehybridization of the carbon atom from sp^2 toward sp^3. From the interpretation of HREELS spectra for molecularly adsorbed ethylene on Rh(111) and Rh(100) Bent et al. [9] have proposed that a general correlation may exist between the vibrational frequencies in deuterated ethylene spectra and the C–C stretching force constant in adsorbed C_2D_4. With the help of this correlation, a C–C bond order of 1.5 for ethylene adsorbed on Rh(111) has been estimated (table 1). Stronger rehybridization occurs on Rh(100) as indicated by the bond order of 1.2 (table 1). The frequency of the C–C stretching vibration of molecularly adsorbed C_2D_4 could not be observed in the present case due to the strong absorption of the silica support below 1300 cm^{-1}. However, based on the comparison of the C–H stretching modes, as listed in table 1, we suggest a degree of rehybridization of ethylene on Rh/SiO_2 between that for π- (bond order 1.7 [7]) and di-σ- (bond order 1) bonded C_2H_4.

The molecularly adsorbed ethylene C_2H_4(ads.) rapidly reacts with hyrogen at room temperature as evidenced by spectrum d in fig. 1. Upon admission of 10 mbar H_2 the peaks due to C_2H_4(ads.) immediately disappear. Surprisingly, at the same time the intensities of the ethylidyne peaks decrease substantially. Two poorly resolved new bands appear in the C–H stretching region at 2958 and



Scheme 1.

2939 cm^{-1} together with two additional peaks at 1460 and 1381 cm^{-1}. The new features seem to disappear partially on subsequent evacuation, whereas the set of ethylidyne bands grows again in intensity with increasing time of evacuation (spectra e and f in fig. 1). However, the initial intensities of the ethylidyne peaks cannot be restored. Repeated H_2 admission and evacuation causes the same phenomena reversibly as shown in spectrum g in fig. 1. We have repeated the cyclic treatments up to five times. This high sensitivity of rhodium ethylidyne to hydrogen was unexpected and is different from results previously found on Rh single crystals. One possible explanation for the influence of H_2 on the spectra shown in fig. 1 is the partial hydrogenation of the ethylidyne to form surface ethyl groups in a reversible reaction,

$$Rh_3CCH_3 \underset{+H_2}{\overset{-H_2}{\rightleftharpoons}} Rh\text{-}CH_2CH_3 + 2Rh.$$

Ethyl fragments, which undergo the reverse reaction, have been discussed as intermediates in one of the mechanistic concepts of ethylidyne formation from ethylene [8]. The elementary steps of this dehydrogenation reaction are not very well understood. Three concepts, which basically differ in the type of the initial step, are illustrated in scheme 1.

Somorjai et al. [8] have suggested a hydrogenation/dehydrogenation mechanism (I), in which molecularly adsorbed C_2H_4 initially undergoes hydrogenation to ethyl, followed by stepwise dehydrogenation at the α-carbon to form ethylidyne via ethylidene species. This reaction mechanism is energetically favoured as shown by a combination of molecular orbital calculations for a Pt(111) surface [17] and experimental measurements on Pt(111) [18].

An alternative concept (mechanism II), in which the ethylidene ($-CHCH_3$) groups are assumed to result from an intramolecular hydrogen shift in adsorbed ethylene, does exclude ethyl species as intermediates in ethylidyne formation [19].

Other proposals (mechanism III) are based on the assumption that ethylene conversion to ethylidyne is initiated by dehydrogenation to form vinyl species, followed by further dehydrogenation to vinylidene ($=C=CH_2$) [20]. Finally,

Table 2
Vibrational frequencies (in cm^{-1}) of ethyl fragments as intermediates on Pt and Rh surfaces

Surface	$\nu_{as}(CH_3)$	$\nu_{as}(CH_2)/\nu_{sym}(CH_2)$	$\nu_{sym}(CH_3)$		$\delta_{as}(CH_3)$	$\delta_{sym}(CH_3)$	Ref.
Pt/SiO_2	2957	2939	2870	2859	1468	1383	[14]
Rh/SiO_2	2958	2939	–	–	1460	1381	this work
Pt/Al_2O_3	–	–	–	–	1475	1360	[13]

rehydrogenation was assumed to lead to the formation of ethylidyne. Alternatively, an intramolecular hydrogen shift in the vinyl intermediate may directly give ethylidyne [21].

Ethyl groups are only involved in the hydrogenation/dehydrogenation mechanism I. Apart from ethylene adsorption, the decomposition of propionaldehyde or alkyl halides has been examined in view of the formation pathway of ethylidyne: ethyl species, formed by low temperature decarbonylation of propionaldehyde on Rh(111), have been postulated to dehydrogenate to give ethylidyne [22]. However, the participation of $-C_2H_5$ in ethylidyne formation is still under discussion. Athough ethyl iodide adsorption on Pt(111) at room temperature generates ethylidyne, C_2H_5I adsorption at low temperature revealed that ethyl groups pass directly to di-σ-adsorbed ethylene at 200 K, which decomposes around 300 K to form ethylidyne [23]. In contrast, our results for silica-supported rhodium rather support a direct interconversion between ethyl and ethylidyne, adsorbed on highly dispersed rhodium at room temperature. The wavenumbers of the bands which appear upon H_2 admission at the expense of the ethylidyne peaks agree very well with those previously assigned to ethyl groups on Pt/SiO_2 [14] (table 2). Because ethylidyne species are always present in our case, the symmetric stretching modes of CH_3 and CH_2 are superimposed by the intense symmetric stretching vibration of the ethylidyne methyl groups. Evidence of an ethyl group with CH_3 deformation vibrations at 1360 and 1475 cm^{-1} has been found on Pt/Al_2O_3 during hydrogenation of a "dehydrogenated" surface species with the proposed structure "M–CH–CH–M" at 247 K [13] (table 2). The "dehydrogenated" species was characterized by a peak at 1337 cm^{-1} which has been attributed to the CH deformation mode. In the light of today's knowledge of infrared spectra of ethylidyne adsorbed on platinum, the spectrum should be reinterpreted and the 1337 cm^{-1} peak should be assigned to the symmetric deformation mode of the methyl group in Pt_3C-CH_3. When hydrogen was admitted to Pt ethylidyne, the band decreased in intensity and the C_2H_5 peaks grew in. The ethyl intermediates were entirely hydrogenated to ethane at 253 K in hydrogen atmosphere on Pt/Al_2O_3 [13]. In the present case, the conversion of Rh_3CCH_3 into gaseous ethane on Rh/SiO_2 is complete only upon hydrogenation at 373 K.

3.2. Rh–VO_x/SiO_2

The spectra, which have been obtained upon admission of 11.5 mbar C_2H_4 onto Rh–VO_x/SiO_2 at 300 K are shown in fig. 2. Spectra 2a–2d have been recorded in the presence of C_2H_4 in the gas phase. Immediately upon C_2H_4 admission three bands of adsorbed species at 2924, 2853 and 1468 cm^{-1} appear (spectrum a in fig. 2). With increasing time an additional peak grows at 1381, the peak at 2924 becomes broader and some additional feature may be covered by the adsorption bands of gaseous ethylene (spectra b–d in fig. 2). After 20 min treatment with C_2H_4 at room temperature and subsequent evacuation, peaks at 2966, 2924, 2853, 1381 and a broad band around 1460 cm^{-1} remain in the spectrum (spectrum e in fig. 2).

The band pattern in spectrum a in fig. 2 may be attributed to the antisymmetric and symmetric stretching vibrations and the deformation vibrations of methylene species adsorbed on rhodium particles. The spectrum implies that the dissociative adsorption of C_2H_4 happens on Rh–VO_x/SiO_2 in an unusual way via C–C bond scission. Because C–H bond breaking occurs at lower temperatures than C–C bond breaking, it is generally assumed that ethylene decomposition is initiated by dissociation of C–H bonds and the formation of dehydrogenated species like CCH_3 or CCH. Fragmentation of ethylidyne into CH intermediates was observed on Rh(111) only at temperatures higher than 400 K [5]. On Rh(100) ethylidyne is thermally stable up to 380 K. The absence of vibrational modes typical for methyl groups in spectrum a (fig. 2) indicates that the initial step in ethylene decomposition on highly dispersed, vanadium oxide

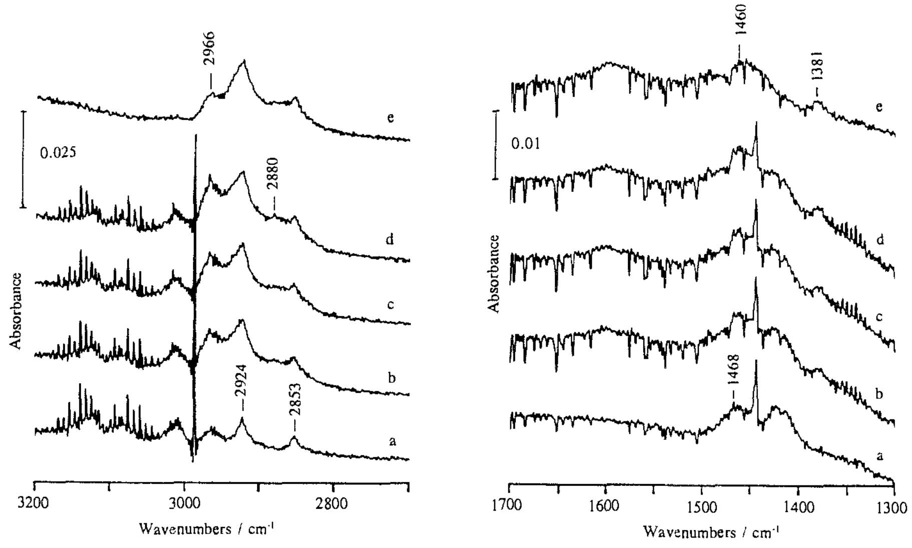


Fig. 2. Infrared spectra of ethylene adsorbed on Rh–VO_x/SiO_2 at room temperature: (a) after exposure in 11.5 mbar C_2H_4 for 60 s; (b) 420 s; (c) 600 s; (d) 900 s; and (e) after evacuation for 300 s.

promoted Rh is the dissociation of the carbon–carbon bond and the formation of methylene groups. Subsequent hydrogenation of the CH_2 fragments may lead to the formation of methyl species as evidenced by the peaks at 2966 and 1381 cm^{-1} in spectrum e of fig. 2. The hydrogen could be delivered by further dehydrogenation of CH_2 or may be present on the surface as residual H_2 from the reduction of the catalyst.

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